

The University of Chicago

A CALORIMETER FOR MEASURING
VERY SMALL HEATS OF
DILUTION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By

CONRAD E. RONNEBERG

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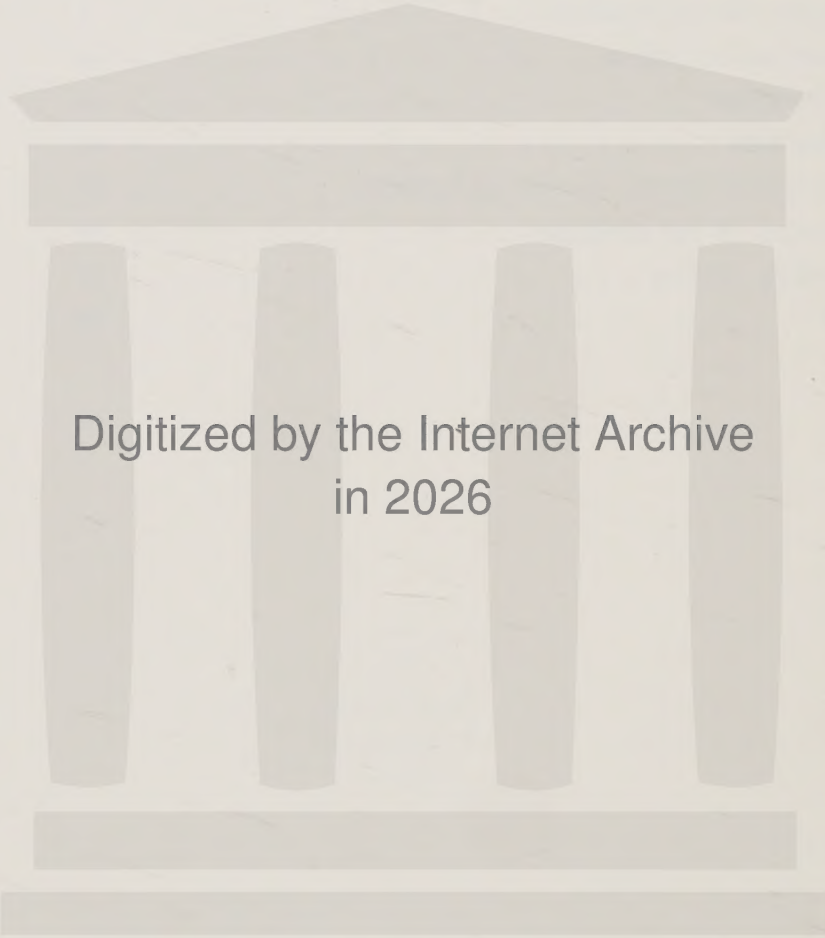
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INTRODUCTION

The precise determination of the heat of dilution of electrolytes, especially in solutions less than 0.10 molal, has become of greater theoretical interest since the advent of the Debye-Hückel theory of interionic attraction. The equations of Debye-Hückel, for instance, make it possible to calculate the various thermodynamic properties of dilute solutions and have, therefore, increased the interest in the concept of the activity coefficient.¹ The equations, furthermore, gave an explanation for the empirical discovery of Lewis and Randall that the activity coefficient depended primarily on the ionic strength of the solutions.² One of the most useful methods for the determination of activity coefficients, the freezing point method, requires a knowledge of the relative partial molal heat contents. Heat of dilution data for electrolytes less concentrated than 0.10 m are needed for the essential extrapolation to infinite dilution required for the accurate determination of the relative partial molal heat contents. Work done since the advent of the Debye-Hückel theory has revealed a change of sign of the heat of dilution at a concentration of about 0.16 m; most of the early evaluation of relative partial molal heat contents are, therefore, seriously in error. Obviously, extrapolation to infinite dilution from concentrations, where the heat of dilution is positive, must

¹Debye and Hückel, Physik, Zeit., 24, 185 (1923); Debye, ibid., 24, 334 (1923).

²G. N. Lewis and M. Randall, "Thermodynamics," The McGraw Hill Book Co., New York, 1923, p. 374.

be seriously in error if there is a change in the sign of the slope of the curve and this change is neglected or overlooked.³

The determination of heats of dilution of electrolytes is one of the direct experimental methods for testing the Debye-Hückel theory. The theory demands that the integral heat of dilution should be proportional to the square root of the ionic strength. In the simple theory,⁴ ΔH^* , the increase in heat content when a solution containing one mole of solute is diluted to infinite dilution, is given by⁵

$$\Delta H^* = \frac{-3}{2} \frac{N \mu^{\frac{1}{2}} \epsilon^{\frac{3}{2}}}{D^{\frac{3}{2}} (kT)^{\frac{1}{2}}} \sqrt{Z n_1 z_1^2} \left[1 + \frac{T \Delta D}{D \Delta T} - \frac{T \Delta V}{V \Delta T} \right], \text{ or} \quad (1)$$

$$\Delta H^* = -A \sqrt{\mu} \quad (2)$$

A in equation 2 is the limiting slope of the curve representing ΔH^* as a function of $\mu^{\frac{1}{2}}$. Lange and coworkers developed methods of calorimetry for the investigation of the extremely small heat effects involved in the dilution of solutions as dilute as 0.01 m. Their work indicates that the integral heats of dilution for very dilute solutions are in the main proportional to $\mu^{\frac{1}{2}}$, and agree fairly well with the limiting slope calculated from the Debye-Hückel theory. Present uncertainties concerning the dielectric constant of water and its temperature coefficient must be removed before better agreement can be expected.⁶

³Cf. Robinson, J.A.C.S., 54, 1311 (1932).

⁴Harned and Ehlers, J.A.C.S., 55, 2188-2189 (1933).

⁵Symbols: N = Avogadro's number; ϵ = charge on electron; D = dielectric constant of solvent; T = absolute temperature; V = volume of solution; k = Boltzmann constant; n_1 = number of ions of the 1th kind per cubic centimeter; z_1 = valence of the 1th ion; μ = the ionic strength.

⁶Lange and Robinson, Chem. Rev., 8, 89-115 (1931).

Workers in this laboratory have been making heat of dilution measurement for sodium chloride down to concentrations of 0.10 m. Young and Vogel have reported measurements at 25° C.⁷ and Machin has worked with sodium chloride at 0°, 12.5°, and 25° C.⁸ To handle heat of dilution data, the chord-area method has been developed in this laboratory.⁹ In this method the function, $\Delta \phi H / \Delta (m^{0.5})$ is plotted against $m^{0.5}$, where ϕH is the apparent molal heat content; i.e., chords instead of points are plotted as a function of $m^{0.5}$. In order to obtain the derivative curve from a plot of chords, mathematical considerations require that the curve be drawn so that the two areas enclosed between the curve, the chord and imaginary vertical lines drawn through the ends of the chord, are equal. The difficulty in such a procedure increases with the length of the chord; i.e., with $\Delta m^{0.5}$.

The only data for solutions approaching 0.01 m are those of Lange, Robinson, and their coworkers.¹⁰ The experiments on sodium chloride solutions by Lange and Robinson were made at 25° C. and yield chords which are much longer than desirable. The present work was undertaken to devise a calorimeter which would make possible the attainment of the following experimental objectives:

1. To extend the heat of dilution experiments of this laboratory to the very dilute range.
2. To measure precisely the function, $\Delta \phi H / \Delta (m^{0.5})$ for relatively small values of $\Delta (m^{0.5})$; i.e., to obtain short chords

⁷Young and Vogel, J.A.C.S., 54, 3030-3040 (1932).

⁸Machin, Thesis, University of Chicago, August, 1932, pp. 18-20.

⁹Young and Vogel, op. cit., 54, 3032 (1932).

¹⁰Robinson, J.A.C.S., 54, 1311-1318 (1932); Lange and Robinson, op. cit., pp. 89-115.

required for precise calculations.

3. To supply an entirely independent check on the work of Lange and coworkers.

Preliminary calculations showed that for solutions more dilute than 0.10 m the energy change of dilution would always be less than 0.10 calorie. Hence, it was necessary to design a calorimeter in which heat effects of less than 0.10 calorie could be measured accurately and in which the molality changes should be relatively small. To attain the first objective, a multiple junction thermel was used to indicate the temperature between the two sections of a divided calorimeter. To attain the second objective, it was merely necessary to arrange for a dilution change small enough for the purpose.

THE THERMEL AND GALVANOMETER

The earlier workers in micro-calorimetry have attempted to get high temperature sensitivity principally by increasing the number of junctions in the thermel.¹¹ This is the proper procedure when the thermel is of the conventional type used to measure large temperature differences and when the resistance of the circuit used to measure the potential is large in comparison with the resistance of the thermel. Under these conditions, the introduction of more couples into the thermel will not materially change the total resistance and the gain in potential obtained as a result of the use of more junctions is a real advantage. When, however, it is necessary to measure very small temperature differences of the order of 1×10^{-6} degree, certain considerations, which will be discussed later, place a limit on the number of junctions that can be used, and, furthermore, difficulties not

¹¹Lange and Robinson, op. cit., p. 102; Hill, Proc. Roy. Soc., Series B, 111, 106 (1932).

ordinarily encountered in work with thermocouples immediately appear. It is impracticable, for instance, to use one of the standard potentiometers to measure the extremely small potentials produced in the thermel, because the parasitic e.m.f.'s in even a well designed potentiometer might approach or exceed that produced in the thermel itself.¹² Instead it is necessary to use a very sensitive galvanometer as a deflection instrument, or an especially designed potentiometer circuit as described below. The necessity for this procedure may be better appreciated if it is pointed out that a copper-constantan thermel with an hundred pairs of junctions subjected to a temperature difference of 1×10^{-6} degrees, will produce a potential of only 4×10^{-9} volts.

The potential measuring circuit must be so designed that the torque on the moving system in the galvanometer is a maximum for a given temperature difference and a given permitted heat loss in the calorimeter. The magnetic field set up within any coil as the result of the passage of a current through it is directly proportional to the number of ampere-turns. In the following discussion concerning the relative sensitivities of galvanometers the actual torques will not be discussed, but merely the number of ampere-turns to which the torques are directly proportional.

The following symbols will be adopted in order to study the factors involved in the design of a combination of a thermel and galvanometer with as large a temperature sensitivity as possible:

D = galvanometer deflection;

G = galvanometer resistance;

I = current through thermel and galvanometer;

¹²White, J.A.C.S., 36, 1858 (1914).

N = number of turns in galvanometer coil;

e = e.m.f. of each couple per degree;

n = number of couples in series in the thermel;

r = resistance of each couple;

k_1, k_2 , etc. = various proportionality constants;

W = length of wire in galvanometer coil;

L = length of one couple.

In any galvanometer, the volume of wire in the coil is determined by the shape and size of the coil. For a given coil the volume of wire can be considered nearly constant. The resistance of the coil, however, depends upon the size of the wire used. The resistance of two coils, wound with wires of different cross-sectional areas and filling the same volume, is proportional to the squares of the wire lengths. Hence,

$$G = k_1 W^2 \quad (3)$$

Since W^2 is proportional to N^2 ,

$$G = k_2 N^2, \text{ or} \quad (4)$$

$$N = k_3 G^{1/2}. \quad (5)$$

The deflection is proportional to the number of ampere-turns; or

$$D = k_4 IN, \text{ or} \quad (6)$$

$$D = k_5 I G^{1/2}. \quad (7)$$

Since $I = ne/(nr + G)$, we can derive from equation 7

$$D = k_5 (ne/nr + G) G^{1/2} \quad (8)$$

If we differentiate equation 8 with respect to G , we obtain:

$$dD/dG = -G^{0.5} (nr + G)^2 + 1/2 [G^{1/2}(nr+G)] \quad (9)$$

The value of G required for a maximum value of D is the value which will make the right hand member of equation 9 equal to zero. For this to be true,

$$G = nr \quad (10)$$

If sensitive galvanometers of various resistances are available, it should be emphasized that there is a distinct advantage in the galvanometer having a resistance as low as possible, since it reduces the number of junctions needed in the thermel. This procedure is quite different from that of many previous workers in this field. Lange, for example, using a galvanometer with a resistance of 25 ohms, employed an iron-constantan thermel of 1072 junctions and resistance of 75 ohms.¹³ Later it will be shown that the limiting factor in obtaining maximum temperature sensitivity is not the number of junctions. The use of few junctions means greater simplicity in design, and makes it possible to pay more attention to the distribution and insulation of the junctions.

The determination of the optimum value of (nr) requires a consideration of such factors as materials for the thermel, wire sizes, heat loss through the thermel, etc. Heat conductivity through the thermel results in a reduction of the temperature difference between the halves of the calorimeter and this must be considered because of its effect on the curvative of the cooling curves. The curvature to be tolerated determines the heat loss which can be permitted and this in turn determines certain characteristics of the thermel. In an actual dilution experiment there will be a change in temperature when a salt solution is diluted. For very dilute solutions heat will be evolved. Consequently, the solution in the working half of the calorimeter will become warmer than its surroundings, and the thermel potential will suddenly rise to a maximum and then fall at a rate which is determined by the rapidity of cooling. Refer to Figure 7. Because of the time necessary to obtain uniformity of the

¹³Lange and Robinson, op. cit., p. 100.

temperature after dilution and for the heat to reach the thermel, there is a certain lag in the measurement of the temperature change. In order to secure the temperature change at the instant of dilution, the cooling curve is extrapolated backward to the time of opening. If there is to be no uncertainty in this extrapolation, it is essential that the cooling curve be nearly a straight line. If the rate of heat transfer to the cooler half, however, is too large, the slope of the cooling curve will change too rapidly.

A knowledge, then, of the permissible rate of heat loss between the halves of the calorimeter is necessary before the characteristics of the thermel can be determined. It was decided that an attempt would be made to allow the rate of heat loss to be such as to cause the change in temperature during each minute to be about two per cent of the prevailing temperature difference. It was further decided that the heat loss should not be permitted to be much larger than that caused by the bakelite partition alone. The larger part of the heat loss, of course, occurs through the bakelite wall between the halves. The heat capacity of the working half is about 400 calories per degree of temperature change. A change in temperature of two per cent during each minute because of heat transfer through the partition and thermel means a transfer of about four calories per minute if the temperature difference is one degree. The heat conductance of the bakelite partition was calculated from its dimensions, thickness, and the thermal conductivity¹⁴ to be about 3.1 calories minute⁻¹ degree⁻¹. This would mean that only enough metal should be put into the thermel to increase the heat transferred to about 4.0 calories minute⁻¹ degree⁻¹. This limit adopted for the heat loss, admittedly more

¹⁴ Thermal conductivity = 0.0004 cal. deg.⁻¹ sec.⁻¹.
Data furnished by the Bakelite Corporation.

or less arbitrary, was satisfactory in practice, but may be modified slightly in future work on the basis of the experience gained in this research.

A second major consideration in the design of a thermel to be used in the measurement of very small potentials is the amount of current that will be available for operating the galvanometer. For a given heat loss and a given temperature difference, the current should be as large as possible. In brief, then, the ratio of the electrical conductivity to the heat conductivity should be a maximum and this condition requires a selection of certain optimum wire sizes.

Let: a_1 and a_2 = the areas of wires 1 and 2;

k_1 and k_2 = the thermal conductivities;

ρ_1 and ρ_2 = the specific resistances;

H' = heat transferred each minute by each couple for a one degree temperature difference;

H = heat transferred each minute by thermel for a one degree temperature difference;

C = the conductance of one couple.

Then:

$$H' = 1/L (k_1 a_1 + k_2 a_2) \quad (11)$$

The conductance for each couple is C amperes volt⁻¹:

$$C = \left[\frac{a_1 a_2}{a_2 \cdot 1 + a_1 \cdot 2} \right] 1/L \quad (12)$$

Hence,

$$H' / C = \left[(k_1 a_1 + k_2 a_2) (a_2 \cdot 1 + a_1 \cdot 2) \right] / a_1 a_2 \quad (13)$$

Finding $d \frac{H'}{C} / d a_2$, and solving for the minimum, we find that the minimum value of the ratio of the heat loss to electrical conductivity, of a couple will be realized when:¹⁵

¹⁵White, op. cit.

$$a_2/a_1 = \sqrt{k_1 \rho_2 / k_2 \rho_1} \quad (14)$$

Now, if the areas of the wires for a thermel of n junctions are chosen in accordance with this condition, equations 11 and 14 may be combined to give equation 15:

$$nH' = H = (na_1/L) \times \left[k_1 + \sqrt{k_1 k_2 \rho_2 / \rho_1} \right] \quad (15)$$

Also,

$$r = L(\rho_1/a_1 + \rho_2/a_2) \quad (16)$$

From 14 and 16 it follows that

$$n/r = na_1/L \left[\rho_1 + \sqrt{\rho_1 \rho_2 k_2 / k_1} \right] \quad (17)$$

Now, from 15 and 17, we derive:

$$n/r = H / \left[\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2} \right]^2 \quad (18)$$

Examination of equation 18 indicates that the ratio n/r will not change appreciably after the value of H is decided upon, irrespective of the materials in the thermel, unless the denominator of the right hand member of equation 18 changes considerably. The law of Wiedemann and Franz states that the product of the electrical conductivity and the thermal conductivity, in the case of metals, is constant at any given temperature. As a matter of fact, it is also true that this product for alloys, such as constantan, is very nearly the same as the value of pure metals. Hence, it is true that the value of the denominator in the right hand member of equation 18 will not vary over an appreciable range for different materials, which means that the limiting value of n/r will be nearly independent of the materials used to make the thermel.

It should be pointed out that while terms involving the cross-sectional areas do not appear in equation 18, they are implicitly present in H . See equation 15.

Since $nr = G$ (equation 10), we can derive from equation 8

$$D = k_5 (e/2) \sqrt{n/r} \quad (19)$$

If we substitute in equation 19, the value of n/r given in equation 18, we obtain

$$D = \frac{k_5 \sqrt{H}}{2} (e / [\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}]) \quad (20)$$

In this expression, k_5 is a term which is a measure of the sensitivity of the galvanometer. Ayrton and Mather have pointed out, that in order to compare different galvanometers, it is advisable to reduce the deflection per micro-ampere to the values they would have if all galvanometers had unit period and resistance.¹⁶ This value is known as the "factor of merit" of the galvanometer. The deflections are usually expressed in millimeters for a scale distance of one meter. However, instead of divisions per micro-ampere, the deflection may be expressed in divisions per ampere. The factor of merit becomes, then, the deflection per unit current, if the galvanometer also had unit period and resistance:

$$\text{Factor of merit} = D/IT^2G^{0.5}, \quad (21)$$

where T is the period of the galvanometer. Equation 7 states,

$$D = k_5 I G^{0.5},$$

hence:

$$k_5 = D/IG^{0.5}, \quad (22)$$

which when divided by T^2 becomes:

$$\text{Factor of merit} = D/IT^2G^{0.5} = k_5/T^2 \quad (23)$$

Thus, the constant k_5 in equation 20 is numerically equal to the merit factor of the galvanometer multiplied by the square of the period; or, more simply, when T is fixed, k_5 is directly proportional to the factor of merit of the galvanometer.

¹⁶Ayrton, Mather, and Sumpner, Phil. Mag., 30, 58 (1890).

Equation 20 indicates that there are three principal factors involved in the determination of what may be called the overall temperature sensitivity for a combination of a thermel and galvanometer; that is, the deflection per degree change is proportional to the following factors:¹⁷

1. Factor of merit of the galvanometer divided by T^2 ;
i.e., to k_g/T^2 ;
2. Square root of the heat loss through the thermel for a temperature difference of one degree;
3. The ratio: $e / [\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}]$.

This last ratio will henceforth be designated the "merit factor" for the thermel. It is a constant for any pair of metals that may be used for thermel construction, and the value of this ratio should be as large as possible. This single factor takes into account the e.m.f. of the couple per degree, the thermal conductivity, and the resistance for each couple. It is worthy of note that there is no term in equation 20 which mentions directly the number of junctions in the thermel.

The properties of some common metals and alloys, to be considered in the selection of materials for a thermel couple, are tabulated in Tables I and II.

It should be noted that the merit factor for constantan-iron is appreciably greater than for any of the other pairs, and is slightly more than 30 per cent greater than the next best pair, constantan-copper.

Iron and constantan were selected for the thermel used in this research because of the high relative merit factor for this pair. The optimum ratio of the area of the cross-section of the constantan to that of the iron wire in accordance with equation 14

¹⁷ Cf. Whipp, Phil. Mag., 18, 745-759 (1934).

is 3.6 : 1. No. 24 constantan and No. 30 iron wire were selected, which have a ratio of 4:1. The calculated heat loss per degree

TABLE I
PROPERTIES OF THERMEL MATERIALS

Material	Thermal Conductivity cal. cm. ⁻¹ deg. ⁻¹	Specific resistance ohm cm. x 10 ⁶
Iron	0.161	10
Copper	.918	1.77
Constantan	.054	44.6
Platinum	.166	10
Platinum, 10% iridium	.074	24
Platinum, 10% rhodium	.074	21.4

temperature difference for one couple of these wires 1.5 cms. in length is 0.0077 calories per minute. As has been explained before, the number of junctions is determined by the permissible heat loss through the thermel. The permissible heat transfer per

TABLE II
PROPERTIES OF THERMEL PAIRS

Thermel pairs	E.m.f. deg. ⁻¹ junction ⁻¹	Merit Factor x 10 ³
Constantan, copper	40 x 10 ⁻⁶	14.2
Constantan, iron	52.5 x 10 ⁻⁶	18.4
Platinum, platinum-iridium	13.2 x 10 ⁻⁶	5.02
Platinum, platinum-rhodium	7.01 x 10 ⁻⁶	2.77

minute through the thermel was 0.90 calorie per degree temperature difference. Hence, $n = 0.90/.0077$ or 120 junctions. The thermel, as built, actually consisted of 100 couples in series, and had a resistance of 8.3 ohms.

As has been explained before, the rate of heat transfer through the bakelite partition for a temperature difference of one degree was about 3.2 calories. The presence of 120 junctions would bring the heat loss to about four calories per minute. If an attempt had been made to increase the temperature sensitivity by a factor of two, the heat loss due to the thermel alone would have been increased four times. See equation 20. If the same size of wire were to be used, the number of junctions would have to be increased to 480. Not only would the construction of such a thermel have been a very laborious procedure, but the heat loss would have been increased 60 per cent, which undoubtedly would have introduced greater curvature into the cooling curve.

A Paschen galvanometer, made by the Cambridge Instrument Company, was selected because there is no other instrument with a larger galvanometer factor of merit.¹⁸ This is an instrument with a moving magnet system of two groups of five very small permanent magnets, with a weight of thirty milligrams, fastened to a fine glass stem, which is suspended by a quartz fiber twenty cms. long and about one millimicron in diameter. The current sensitivity is as high as 7×10^{-11} amperes per millimeter deflection at a scale distance of one meter. The period and the sensitivity can easily be varied by a pair of adjustable control magnets and the damping is not materially affected by the resistance of the circuit. As ordinarily used, the sensitivity was about 02.0×10^{-10}

¹⁸ The factor of merit is 20,000, according to The Cambridge Instrument Co.

amperes/mm./m. The coils may be connected in series, series-parallel, or parallel, so that the resistance of the instrument can be varied over a wide range.¹⁹ As used, the coils were in series, which made the galvanometer resistance 12 ohms. The location of the thermel in the dividing wall permitted each couple to be very short, about 1.5 cms., and this resulted in a resistance for the hundred junctions of only 8.4 ohms. While this resistance resulted in a departure from the ideal relationship, $nr = G$, the loss in galvanometer sensitivity was only about 3 per cent.²⁰

The thermel was insulated with four coats of the varnish used to insulate electric wire²¹ and was then submerged in a bed of picein. The picein was poured, when melted, into special temporary forms, one on each side of the partition. The wax was kept in liquid form for a period of four hours in an oven at 130° C. to allow time for any entrapped bubbles of air to rise to the surface and permitted the formation of a solid mass of picein when it was allowed to cool. The layer of picein was finally shaped by the removal of the excess picein. A layer one millimeter thick was left over the ends of the junctions.

Unusual precautions had to be adopted to realize those conditions which allowed the galvanometer to function consistently. The principal difficulties were the following: vibrational and mechanical disturbances, magnetic effects, thermo-electric effects in the wires, and electrical leakage into the galvanometer from outside sources.

¹⁹Paschen, Mendenhall, Waidner, and Abbott, Phys. Zeit., 14, 521-524 (1913).

²⁰Brooks, B. of S. Jour. of Res., 4, 297 (1930).

²¹The varnish was baked in place at about 140° C. as recommended by the Belden Wire Co., the manufacturer.

The galvanometer was placed on a heavy stone block which rested on thin pads of gasket rubber placed on a stone slab, which, in turn, rested on a heavy foundation made of iron pipe. This mounting reduced vibrational disturbances to eliminate uncertainties in the observations.

Thermo-electric effects were largely eliminated by the use of copper for all wires, binding posts, and other parts of the circuit. There was only one soldered connection, and this was carefully lagged with a large roll of cotton to prevent rapid changes in its temperature.

The galvanometer was shielded against magnetic effects with an outer shield of soft iron and an inner shield of "mu metal." Shielding other than that built into the instrument proved to be unnecessary. Mu metal is an alloy with a very high permeability and is very effective against weak magnetic fields. For this reason it was located inside the iron shield to absorb any magnetic flux that might pass through the iron to the interior. The sensitivity of a Paschen galvanometer is so high that it responds to the very weak currents produced by a change of the intensity of the magnetic field in the laboratory if the wires of the galvanometer circuit are separated as in ordinary practice. Trouble from this source was reduced to a safe minimum by the twisting of all wire pairs together to avoid magnetic loops. Where it was impossible to avoid a magnetic loop, its effect was neutralized by the addition of another loop which would produce an opposite and equal e.m.f. when the magnetic field changed. There are, for example, loops built into the galvanometer base. Opposing loops which would set up an opposite e.m.f. were therefore placed beneath the galvanometer.

The galvanometer potentiometer system was placed on a

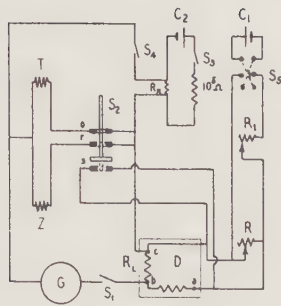


FIGURE 1



FIGURE 3

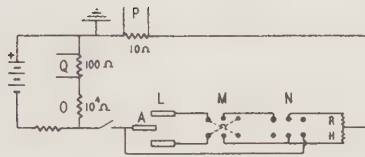


FIGURE 4

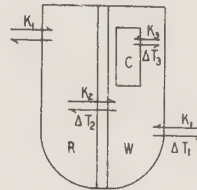


FIGURE 5

Fig. 1.-- The potentiometer system.

Fig. 3.--The dilution vessel.

Fig. 4.--The electrical calibration system.

Fig. 5.--Various paths of heat flow within calorimeter.

single copper equipotential shield, which rested upon thick pieces of bakelite to isolate it electrically. This ensemble had no connection to the earth. There were a number of places where unusual precaution had to be taken to avoid electrical leakage into the galvanometer circuit. The galvanometer circuit was adjacent to a second electrical measuring circuit which was necessary to determine the heat capacity of the calorimeter and contents, shown in Figure 4. This auxiliary circuit was also placed on a separate equipotential shield connected to the ground to isolate it electrically from the galvanometer circuit.

The galvanometer was used as a null point instrument so that with frequent determinations of the zero point, parasitic e.m.f.'s of any kind in the circuit had no influence on the reliability of the results. The steadiness of the zero point, except on a very gusty day, was very satisfactory. The zero point usually did not "wander" over a distance of more than one-half of a centimeter on the galvanometer scale and this change usually occurred as a slow drift. This shift in the zero point had little effect on the reliability of the readings since the zero point was determined at least once every minute during the observation periods.

THE POTENTIOMETER SYSTEM

The potentiometer system is diagramed in Figure 1. R_1 is a standard four dial resistance box which was varied from 3000 to 10,000 ohms; R is a similar resistance box variable in steps from 1000 ohms down to 0.10 ohm. D is a potential divider constructed entirely of copper. The resistance from a to c is about 10,000 times that from b to c , which is labelled R_L on Figure 1. The total resistance of the divider was 35.53 ohms.

White has shown that it is difficult and unnecessary to

keep a circuit with a very sensitive galvanometer entirely free of stray electromotive forces, or so-called "parasitics."²² It is sufficient to make them very small in comparison with the voltages to be measured and to arrange the circuit so that their presence will not affect the reliability of the measured potentials. The apparatus provided for this purpose is shown in Figure 1. Z is a coil of copper wire non-inductively wound of the same resistance as the thermel T. The switch S_2 has two positions: In one position, the contacts o were open and contacts r and s were closed. The resistance of the circuit through s was so low that any potential from the cell C_1 impressed upon the galvanometer was negligible. The galvanometer deflection was then due to parasitics in the galvanometer circuit, and was taken as the galvanometer reference point or zero reading. To obtain a thermel reading, a single movement of the switch caused the following sequence of operations: First, the circuit at r was opened, then the contact at s was opened, and finally the thermel circuit was closed at o. In this last position, the thermel was in the galvanometer circuit, and R and R_1 were varied to bring the galvanometer to the zero point. The potential drop between b and c was then calculated from the values of R_1 , R and R_L . This potential, of course, is the potential of the thermel.

The switch S_2 may be said to eliminate two potentials in order to get the zero galvanometer reading, namely, the potential in the thermel, and that caused by the cell C_1 in the potentiometer circuit. This switch, therefore, will be referred to as the eliminator switch. An earlier type of eliminator switch gave trouble from time to time, because it permitted some leakage. The trouble was finally attributed to leakage from the circuit passing

²² White, op.cit., pp. 1859-1861.

through the contacts s into the adjacent circuits passing through the contacts o and r. The potential in the s circuit, though never greater than five millivolts, was always from five thousand to fifty thousand times (10,000 times if the thermel potential was approximately balanced) as large as the potential in the o or r circuit. In the first eliminator switch, the binding posts for the high potential circuit were adjacent to the binding posts for the low potential circuit on the bakelite top of the switch. Dust gradually accumulated at this point and apparently allowed leakage into the galvanometer circuit.

In the second eliminator switch, these two circuits were insulated and shielded from each other in the following manner: The contacts o and r were mounted through the bottom of a bakelite cup, which was placed on a metal plate connected to the equipotential shield. The contacts s were mounted in a similar manner in a second bakelite cup placed on the same grounded plate. Leakage from the high potential existing at the contacts s therefore had to pass into the shielding system and was not able to get into the galvanometer circuit. The contacts in the switch S_2 were made with heavy copper bar so that the areas of contact were very large. These contacts were carefully fitted and polished to reduce friction. The original design contemplated the use of oil in the bakelite cups to immerse the contacts. However, thermoelectric effects produced by rapid manipulation of the switch when lubricated with vaseline caused no significant change in the galvanometer reading. The use of vaseline, therefore, was continued. A carefully fitted metal cover was placed over the whole switch to keep out dust. The switch S_1 was a copper knife switch operating in oil.

To test the sensitivity and reliability of the system, provision was made for impressing a very small, known potential

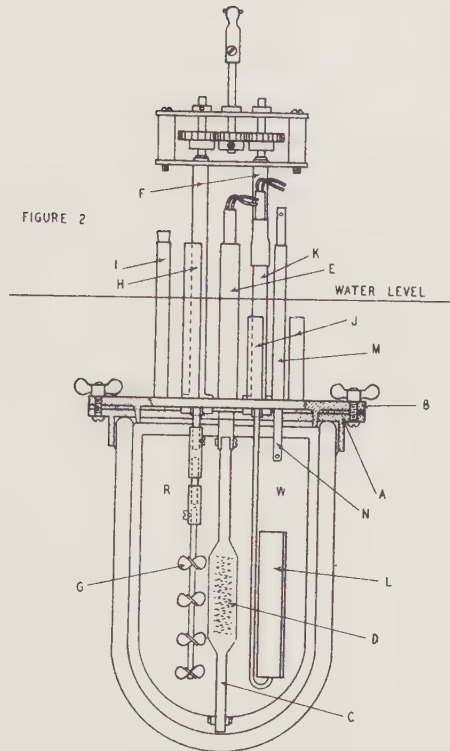


Fig. 2.--The calorimeter.

upon the potentiometer. R_x was an all-copper resistance of about 0.01 ohm, which was kept in a large dewar flask. It was in series with 10^5 ohms, as shown in Figure 1. When the thermel T was disconnected and the switch S_3 was closed, a potential of about 1.5×10^{-7} volts was impressed upon the galvanometer. The precise value of this known potential depended upon the resistance of R_x and the voltage of the cell C_2 . However, knowledge of the absolute accuracy of the potential measured was not needed since only differences in potential were important. This testing circuit was used from time to time to check on the sensitivity and reliability of the whole potentiometer circuit. The potential of the cells C_1 and C_2 were determined with a precision voltmeter or a potentiometer.

THE CALORIMETER

The outer vessel was a large silvered dewar with straight sides. Its depth in the center was about 19 cm. and its internal diameter was 11.5 cm. The dewar was fastened by litharge-glycerine cement to a flanged brass collar A to which the brass cover B was fastened by winged nuts. See Figure 2. The calorimeter vessel proper was inside the dewar. It was made of copper in two halves, R and W, which were fastened by small bolts to the bakelite dividing wall C carrying the 100 junction thermel D. The copper leads from the thermel were carried to the exterior through a glass tube, which was fastened by a brass support at the top of the bakelite partition. This glass tube passed through a brass chimney E in the center of the brass cover. The joints between the copper halves and the bakelite partition were made liquid tight by the use of a gasket made of blotting paper soaked in melted paraffin. While the paraffin was still liquid, the two halves were screwed tightly together. The sharp corners

between the middle partition and each copper half were filled with paraffin. This filler promoted smooth circulation of the liquid. The two vessels held about 410 ml. each.

The electrical leads and the stirrers were inserted through brass chimneys. The shafts for the two stirrers C (only one shown in diagram) were supported by the chimneys F, one over each half. Heat loss along the propeller shaft was reduced by the insertion of a piece of glass rod as a connection between the metal stem of the stirrer and the metal drive shaft above. Over the reference half R, a chimney H carried one arm of a U-shaped thermel (not shown) to determine the temperature of the interior of the calorimeter as compared to the bath. The reference end of the thermel was placed in a dewar filled with water at the temperature of the thermostat in which it was immersed. The chimney I was used to introduce an auxiliary heater or a cooling device, if the temperature of the liquids was far removed from the bath temperature at the beginning of the experiment. For example, when the room temperature at the time the two halves of the calorimeter were filled was considerably below bath temperature, the water and solution, originally at the temperature of the bath, 25° C., cooled somewhat during the time necessary to fill and seal the calorimeter and to transfer it to the bath. The small electrical heater was then used until the temperature of the reference half was as much above bath temperature as it had initially been below bath temperature. The heater was then removed. When half the added heat had been transferred from the reference half to the working half, both were approximately at the temperature of the bath. This procedure shortened by a matter of hours the time necessary for reaching thermal equilibrium within the calorimeter. If the calorimeter temperature became warmer than 25° C. during filling, a cooler,

which consisted of two concentric tubes, was introduced. A continuous stream of cold water passed downward through the inner tube and upward through the outer.

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Over the working half were two short chimneys which held the glass rods used to support the metal dilution pipette, and a chimney K, which supported a platinum heater L. Another chimney M carried a bakelite rod N used for opening the metal pipette.

The platinum heater, with a resistance of about 900 ohms, was of the type described by Groenier.²³ The tube which carried the heater leads and which also acted as the support for the heater was platinum alloyed with 20 per cent iridium. Such an alloy has only 30 per cent of the thermal conductivity of pure platinum.²⁴

The diluting vessel was machined from a solid copper rod 4 cm. in diameter, as shown in Figure 3. The valves which were carried on a support rod of monel were beveled in the lathe and ground in their seats with fine pumice powder. The pipette was supported with platinum wire fastened to two vertical glass support rods, one on each side. The glass rods were held in place in the calorimeter cover by two brass knurled nuts. Thin vaseline was used on the valve seats. A small amount of liquid paraffin was used to make a liquid tight seal around the upper plug and the monel stem.

All the metal parts in the calorimeter were made of copper or monel. The metal parts in the working half were protected from action of the solutions by a heavy coating of gold, which was backed by a layer of silver on an electroplated layer of copper. To clean the stirrers preparatory to coating with copper, they were

²³Groenier, Thesis, University of Chicago, August, 1931, p. 17.

²⁴Int. Crit. Tables, 5, 225.

made anodes in a salt solution for a few minutes and then placed in a strong cyanide solution. The silver and the gold were deposited in a series of layers with a vigorous buffing between each layer in order to obtain a firm coherent coating of each metal.

There must always be some production of heat within the calorimeter due to the friction of stirring. To prevent this heat effect from being a disturbing factor, it was essential that the heat of stirring be made constant. To accomplish this, both stirrers were rotated at the same speed, about 200 r.p.m. by a small 10 watt synchronous motor. All the power was transmitted from the motor to the stirrers by gears.

The thermal leakiness of the whole calorimeter was exceptionally low. The leakage constant ($-K_1$) was found to be 0.0025 minute⁻¹. This constant is defined by the following relationship:

$$d\Delta T/dt = -K_1\Delta T, \quad (24)$$

where ΔT stands for the temperature difference between the interior and the bath, and t represents the time in minutes. Because of the fact that the inner vessel of the calorimeter was independent of the dewar vessel and surrounded by air, this leakage constant is about 60 per cent as large as in the case of Lange's calorimeter.²⁵ The leakage constant was so small that a period of four and a half hours was necessary to dissipate 50 per cent of any given temperature difference between the interior and the exterior of the calorimeter. The constancy of temperature of the bath was ± 0.0001 degree. From the leakage constant it can be calculated that the temperature fluctuations in the contents of the calorimeter would be of the order 0.20×10^{-6} degree if the temperature difference were to persist as long as a minute. In actual experiments the temperature difference of 0.0001 to 0.0002

²⁵Lange and Robinson, op. cit., p. 102.

degree never did last more than a few seconds so that the fluctuations in the temperature of the interior were negligible. It might be pointed out further, that the slight variations in the temperature of the interior that did occur would have little effect on the potential of the main thermel since the changes in the two halves of the calorimeter were approximately equal.

THE OUTER BATH

The temperature of the environment of the calorimeter was controlled by the use of a water bath covered by a double-walled hood made of insulating board. The thermo-regulator, which was placed at one side of the bath, was constructed of nickel tubing, 7.3 meters in length and 1 centimeter internal diameter, bent in the form of a helix and filled with mercury. The head of the regulator was a glass capillary with a make and break device which actuated a relay, which, in turn, operated a 100 watt electric heater lamp. The response of the regulator to very small temperature changes was exceedingly rapid, so that the relay was continually chattering and the heater lamp was not on or off more than a small fraction of a second. The constancy of the bath was checked in the following manner: One end of a conventional U-shaped thermel was placed within the calorimeter, the other end in the water bath near the center. The terminals of the thermel were connected directly to a White potentiometer so that the e.m.f. of the thermel could be measured to hundredths of a microvolt. A series of readings was made which indicated that the temperature was constant to about 0.0001°C . The bath was then allowed to operate four hours with no attention. Three series of five readings each at minute intervals with a waiting period of five minutes between each series of readings were then made. Then after a lapse of thirty minutes, a final series of five readings

was made. This test revealed that the variation in temperature from minute to minute over a period of hours was about 0.0001 degree with the maximum variation of about 0.0002 degree. The excellence of this temperature control combined with the very low leakage constant for the calorimeter, +.0025, meant that errors due to heat leakage are negligible.

THE CALIBRATION SYSTEM FOR THE CALORIMETER

Any heat change due to a dilution within the calorimeter was indicated by a change ΔE_T in the main thermel potention. To convert this change to calories, the whole apparatus was calibrated twice during each dilution experiment by the introduction of a known amount of electrical energy. This required a second electrical system to control the length of the heating period and to enable the resistance of the heater, and the current to be determined. The essential parts of this circuit are indicated in Figure 4. The source of current was a six volt storage battery. The heater H was that previously described. R was a coil, the resistance of which was about the same as that of the heater. L was an automatic switch similar to Groenier's modification of White's design.²⁶ At a selected instant the current was switched from the auxiliary coil R into the heater H, and the current allowed to flow long enough to supply the required amount of electrical energy. By a suitable combination of switch positions for L, M, and N, the same switch was used to stop the current at the required time.²⁷ P and Q were standard resistances of 10 and 100 ohms, respectively. The drop in potential over these resistances was measured on a Leeds and Northrup Model 7552

²⁶White, Phys. Rev., 31, 688 (1910).

²⁷Cf. Groenier, op. cit., p. 13.

potentiometer. The current in amperes flowing in either R or H is one-tenth of the potential drop in volts over the resistance P. The resistance of the heater or auxiliary is equal to $1000 Q/P - 10$. The resistance of the leads is entirely negligible in comparison with the resistance of the heater.

MANIPULATION OF THE APPARATUS

A weighed amount of the solution to be diluted, about 370 ml., was placed in the working half of the calorimeter and a weighed amount of water introduced into the dilution vessel. Both liquids had been brought previously to the temperature of the bath. About 410 ml. of the solution was then placed in the reference half of the calorimeter. The calorimeter was sealed and then carefully lowered into position in the bath. Stirring was started and after a period varying from fourteen to eighteen hours, a condition of thermal equilibrium within the calorimeter was reached as indicated by steady reading on the main thermel. Experiment proved that in order to reach such a steady state, it was necessary that the temperature of the air above the bath remain constant. This condition was realized with the double-walled cover already referred to over the top of the thermostat. Provision was made for opening the metal pipette by a lever mechanism, which was operated from the outside and made it unnecessary to open the cover until the end of an experiment. The use of such a cover was found to be necessary as the calorimeter contents were found to change in temperature as much as 0.00050 degree with a change in temperature of the room, even when there was no perceptible change in the temperature of the thermostat.

To save time in attaining thermal equilibrium within the calorimeter, the small auxiliary heater or cooler already referred to was used just after the calorimeter was placed in the bath,

when either half was found at the start to be far removed from what should eventually be the equilibrium temperature inside. The heater or cooler was always removed after using it.

After an apparent steady state had been reached within the calorimeter, readings on the main thermel were continued for at least an hour to be sure that equilibrium had been attained. The potential of the main thermel was then recorded at minute intervals, on the minute, alternating with readings of the zero point of the galvanometer on the half-minute. If the thermel reading was steady over a period of twenty minutes, the diluting pipette was opened and the readings continued for another period of about twenty minutes. The automatic clock switch was then manipulated to cause the current to flow through the heater H for a suitable period of time, usually sixty seconds. Readings on the main thermel continued without interruption for another period of about twenty minutes. Two of these calibration heater experiments were made during the course of any one dilution experiment. A complete dilution experiment, therefore, required a series of temperature readings before the actual dilution, a series just after the dilution, and two electrical calibrations, each with a series of temperature observations. Each of the four series required fifteen to twenty minutes. Refer to Figure 7.

About the time the main thermel potential became steady, the switch A in Figure 4 was manipulated to cause the current to flow through the resistance R, which was within one-tenth of a per cent of the resistance of the heater, to allow the current for the heater to become steady. The steadiness of current was always ascertained from measurements of the potential drop over P and Q. The amount of current used in the heater was so small, three milliamperes, that there was no difficulty in obtaining a steady current

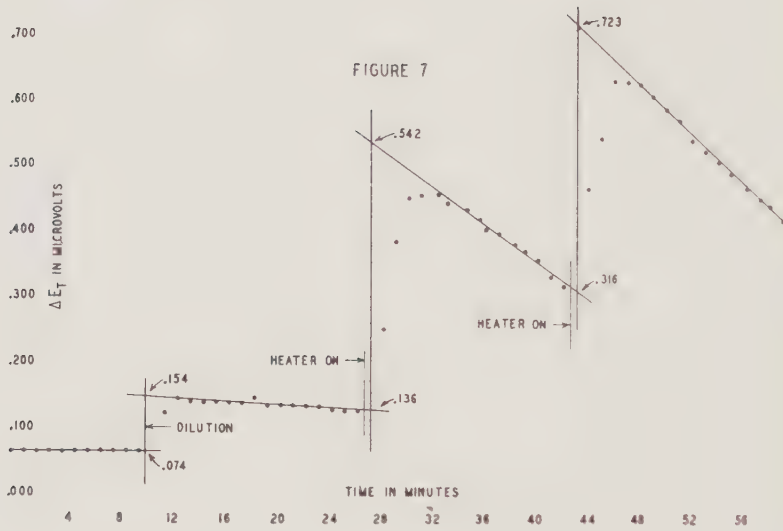


Fig. 7.--Record of a dilution experiment.

within a period of an hour after the current started to flow. At the conclusion of the two calibration experiments, the current was switched into the heater again to measure the drop in potential over resistance P and Q, while the heater was in the circuit. From these two potentials, the magnitude of the current used in the heater and the heater resistance was calculated for that particular dilution experiment. A sample record of a dilution experiment follows. Refer to Figure 7.

Experimental data:

Molality of solution:	0.01925 ₁ m
Weight of solution used:	39.527 g.
Weight of water used:	373.140 g.
Change in potential of thermel after dilution from a plot ΔE_d :	+0.080 mv.
Change in potential ΔE_1 first calibration:	+ .406 mv.
Change in potential ΔE_2 second calibration:	+ .407 mv.
Drop in potential over resistance P:	0.031544 volt
Drop in potential over resistance Q:	.029280 volt
Length of time for current in heater:	60.00 sec.

Calculations:

A. Weight sodium chloride in 1000 g. of water: 0.01925 ₁ x 58.455 =			1.1253 g.
Sodium chloride used: $\frac{39.527}{1001.13} \times 0.01925 =$			0.00076003 mole
Sodium chloride used: 0.00076003 x 58.455 =			0.044428 g.
Water in solution: 39.527 - .0444 =			39.483 g.
Water in final solution: 373.149 + 39.483 =			412.623 g.
Final molality: 0.00076003 x $\frac{1000}{412.623} =$			0.0018419
$\mu_1 = 0.01925_1$	$\mu_1^{0.5} = 0.013875$		
$\mu_2 = 0.0018420$	$\mu_2^{0.5} = 0.042919$		

$$\Delta(\mu^{0.5}) = -0.09583$$

B. Resistance of heater: $R_H = 1000 \text{ } \Omega / P - 10$

$$= 1000 \times \frac{0.029280}{0.031544} - 10$$

$$= 918.23 \text{ ohms.}$$

Current through heater: $I_H = 0.10 \text{ (P)} = 0.0031433 \text{ amperes}$

Heat input during each calibration = $R (I_H)^2 t / 4.185$

$$= \frac{918.23 \times 0.0031544^2 \times 60.00}{4.185}$$

$$= 0.13099 \text{ calories}$$

Mean change of thermel after addition of heat energy:

$$(.406 + .407) / 2 = 0.4065 \text{ mv.}$$

ΔE_T per calorie: $0.4065 / .13099 = 3.1033 \text{ mv.}$

ΔH of dilution: $+0.080 / 3.1033 = -0.02578 \text{ calories}$

$\Delta \phi_H$ per mole: $0.02578 / .0007601 = -33.920 \text{ calories}$

$$\frac{\Delta \phi_H}{\Delta(\mu^{0.5})} = \frac{-33.90}{-0.09583} = +353.9$$

A problem of fundamental importance in the determination of the heat of dilution concerns a possible heat of opening of the dilution pipette. Machin, using a silver capsule with the top and bottom sealed with a thin layer of paraffin, reported a negligible heat of opening.²⁸ Lange attempted to cancel out any heat of opening by placing dilution vessels of similar design in both halves of the calorimeter, and opening them simultaneously. He assumed the two heat effects would cancel each other. If this assumption is valid, a dilution vessel in the reference half is unnecessary, since the constant heat of opening may be determined and applied as a correction. Lange believed that the diluting water was always lower in temperature than the solution outside,

²⁸ Machin, op. cit.

because of the lag in the transmission of heat of stirring, which caused a slight cooling effect when the pipette was opened.²⁹ Early experiments with water, both inside and outside the pipette, indicated that the heat of opening could be zero, positive, or negative. The following analysis of the various paths of heat flow within the calorimeter indicates why such a variation in the heat of opening should be expected.

There are three principal paths of heat transfer involved in the problem, namely, that between the contents of the diluting vessel C and the solution in the working half W, that between the contents of the working half W and the reference half R, and that between the interior of the calorimeter and its surroundings. Refer to Figure 5. The thermal leakage constant $-K_1$ for the whole calorimeter was found experimentally to be +.0025. $-K_1$ is defined by the relationship,

$$\frac{d\Delta T_1}{dt} = -K_1 \Delta T_1 \quad (25)$$

In an analagous manner, we can write the expressions,

$$\frac{d\Delta T_2}{dt} = -K_2 \Delta T_2 \quad \text{and} \quad (26)$$

$$\frac{d\Delta T_3}{dt} = -K_3 \Delta T_3 \quad (27)$$

When the rate of stirring and the bath temperature are constant, a condition of thermal equilibrium must eventually be reached in which the heat generated by stirring within the calorimeter is transferred to the surroundings at a constant rate. In this steady state,

$$\frac{d\Delta T_1}{dt} = \frac{d\Delta T_2}{dt} = \frac{d\Delta T_3}{dt} = 0. \quad (28)$$

This means, of course, that the temperature of the entire contents

²⁹Lange and Robinson, op. cit., p. 103.

will gradually approach a final equilibrium temperature, T_f , which will be, for any particular experiment, due to the heat of stirring a definite amount above the temperature of the bath. This final equilibrium temperature will be approached at a rate which can be expressed as follows:

$$\frac{d(T-T_f)}{dt} = -K_1 (T-T_f) \quad (29)$$

The latter expression can be integrated to obtain the following result:

$$(T-T_f) = (T' - T_f) e^{-K_1 t} \quad (30)$$

In this expression, T' corresponds to the temperature at zero time. According to equation 30, a steady state is reached only after infinite time. Practical considerations demand, however, that this ideal state be approached as closely as necessary in the shortest possible time. Suppose that at the time the calorimeter was placed in the bath, the temperature of the water in the dilution pipette and of the solution in the reference and working halves was above the final equilibrium temperature. There is now a steady drift of temperature of the interior toward the final equilibrium temperature. Since the water in the can is not being stirred, there is a lag in its temperature. After infinite time, the contents of both the can and working half will be at the final equilibrium temperature, and there will be no temperature effect when the dilution pipette is opened. However, it is not necessary nor practicable to reach this ideal state, but rather to make the opening when the heat effect is negligible. This temperature change is negligible when the temperature difference between the interior of the pipette and its exterior is so small that the temperature change in main thermel as a result of opening will be smaller than can be measured.

The sensitivity of temperature measurement desired was

1×10^{-6} degrees. Hence, it was essential that the heat produced when the pipette was opened should be considerably smaller than 1×10^{-6} degrees. Since the dilution ratio of the solution in the working half was ten to one, it follows that in order to obtain a temperature of less than 1×10^{-6} degrees when the pipette is opened, that the average temperature of the water in the pipette cannot differ more than 1×10^{-5} degrees from the temperature of the solution outside.

If the initial temperature of the interior of the calorimeter was below the temperature of the bath, there would have been a drop in temperature if the dilution was made before the theoretical state of thermal equilibrium was reached. This analysis indicates, then, that because of the temperature lag in the pipette contents, an actual temperature change should be expected when the pipette is opened, if the condition of true thermal equilibrium within the calorimeter has not been reached. This change may be either a cooling effect, a heating effect, or so small as not to be measurable.

Mr. John Landwehr, of this laboratory, in a Master's dissertation has analyzed this problem in detail.³⁰ He derived the following equation for the calculation of the temperature difference between the dilution can and the working half:

$$\theta_3 - \theta_1 = \frac{K_1}{K_2 (1 + C_3/C_1) - K_1} (\theta_1 - \theta_2) \quad (31)$$

The symbols have the following significance:

- θ_3 = average temperature of the can;
- θ_1 = temperature of the working half;
- θ_2 = temperature of the bath, which is constant;
- K_1 = leakage constant of the calorimeter;

³⁰ Landwehr, Thesis, University of Chicago, June, 1934, pp. 9-17.

K_2 = leakage constant of dilution can;

C_3 = heat capacity of can;

C_1 = heat capacity of working half.

The value of $\theta_1 - \theta_2$ was determined with a four junction copper-constantan glass encased thermel of conventional design, with a rating of 160 microvolts per degree. The potential was read to tenths of a microvolt with a Leeds and Northrup Model 7552 potentiometer. $\theta_3 - \theta_1$ can be approximated indirectly from the temperature change that occurs when the can is opened by multiplication of the temperature change by the ratio $(C_1 + C_3)/C_3$. This temperature change is measured with the 100 junction thermal which had a sensitivity of 1955 microvolts per degree.

The potential change of the 100-junction thermel can be designated as ΔE_T , and the 4-junction thermel potential before opening as E_1 . Substitution of the microvolt ratings of the two thermels, the heat capacities, and the appropriate leakage constant in equation 31 leads to the following approximate relation:

$$\Delta E_T = 0.0036 E_1 \quad (32)$$

This relation can be used to determine just how small the temperature difference between the interior of the calorimeter and the bath must be in order to have a negligible heat effect when the can is opened. If this temperature effect is to be less than 1×10^{-6} degree, which corresponds to a change of about 0.002 microvolts on the main thermel, the working half should be within 0.5 microvolts (0.003 degree) of the bath temperature. In actual experimental practice, the temperature difference between the bath and the interior of the calorimeter was always less than 0.10 of a microvolt (0.00063 degree) for a period of at least two hours before the time for the dilution. Under these circumstances, the temperature change of opening should be entirely negligible.

These conclusions were checked experimentally by the mixing of water with water. The actual opening was not made until the main thermal potential had been steady for at least two hours, and the calorimeter temperature was within 0.10 microvolts of the bath (0.0006 degree). Under these conditions there was no measurable heat effect. The record of one of many such experiments is shown in Figure 6.

EXPERIMENTAL RESULTS

The principal object of this research was to design and build a calorimeter with its associated potentiometer for the measurement of the extremely small temperature effects that occur when an electrolyte as dilute as 0.01 m is diluted with water. Time did not permit the accumulation of a large amount of experimental data. However, in order to develop the method for the measurement of these very small heats of dilution, a series of actual dilutions of solutions of sodium chloride ranging from a concentration of about 0.20 m down to 0.01 m were made. The results of the experiments were recorded in Table III. The initial molality is represented in column one; the initial and final values of $m^{0.5}$ in columns two and three; the change in $m^{0.5}$ in column four; the approximate change in temperature is recorded in column six; and the energy change involved in the dilution in the calorimeter is found in column seven. The change in the apparent molal heat content is placed in column eight, while the chord for the construction of the derivative curve is in the last column.

The initial concentration of the solutions was determined by the weight dilution of a very carefully analyzed solution of sodium chloride which was about one molal. This original solution was analyzed by the sodium chloride residue method as outlined by

FIGURE 6

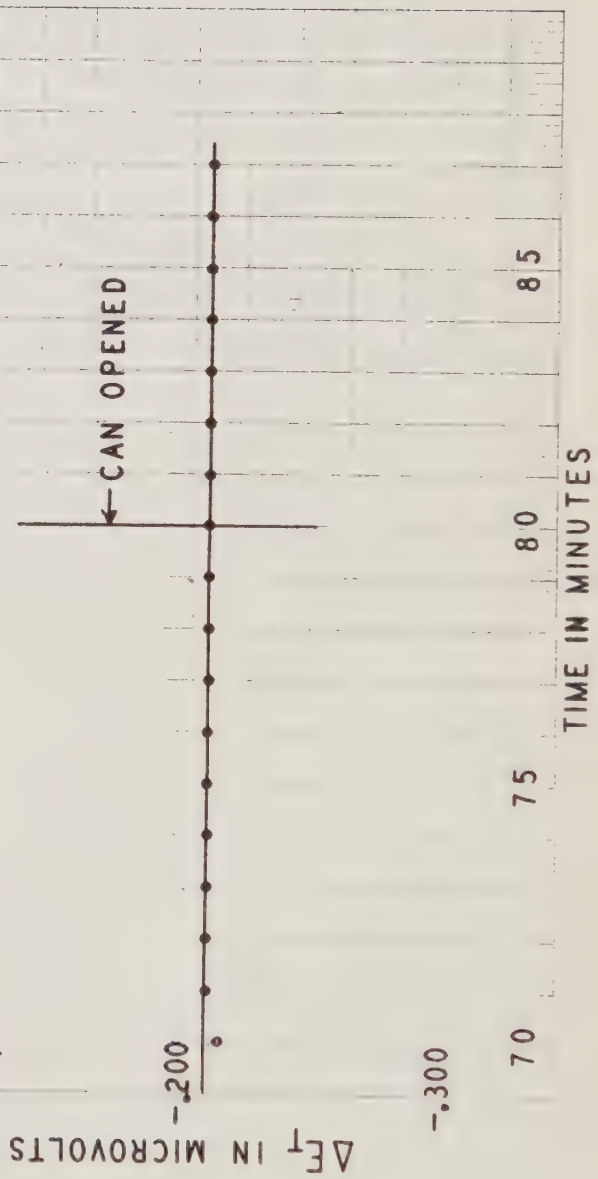


TABLE III
EXPERIMENTAL DATA

m_1	$m_1^{\frac{1}{2}}$	$m_2^{\frac{1}{2}}$	$\Delta(m^{\frac{1}{2}})$	$t^{\circ}\text{C.}$	Δt of dilution	ΔH	$\Delta\phi_H$	$\frac{\Delta\phi_H}{(m^{\frac{1}{2}})}$
0.2056	.45340	.43176	-.02164	24.95	73×10^{-6} deg.	+ .04518	+ .5922	-27.37
0.2056	.45340	.43108	-.02232	24.95	"	+ .04116	+ .5391	-24.15
0.09646	.31058	.29545	-.01513	24.95	"	-.05604	-1.546	+102.2
0.09646	.31058	.29543	-.01515	25.00	"	-.05017	-1.343	+ 88.64
0.04649	.21561	.20779	-.00782	24.98	"	-.02593	-1.491	+190.7
0.04649	.21561	.20620	-.00941	25.10	"	-.0331	-1.887	+200.5
0.01925	.13875	.13194	-.00681	25.00	"	-.01419	-1.978	+290.4
0.01925	.13875	.13196	-.00679	25.03	"	-.01310	-1.823	+268.4
0.01000	.10000	.095180	-.00482	25.08	"	-.006005	-1.596	+331.2
0.01000	.10000	.095145	-.00486	25.05	"	-.006354	-1.690	+348.1
0.01925	.13875	.042863	-.09589	24.98	"	-.02540	-33.49	+349.3
0.01925	.13875	.042919	-.09583	24.98	"	-.02578	-33.92	+353.9

Richards and Hall.³¹ A counter-poise vessel was used to reduce errors due to absorption of water vapor on the sides of the weighing vessel during the weighing. All weighings were reduced to the weight in vacuo. The weights used were carefully calibrated.

The molalities of the various solutions as prepared by the method of weight dilution were checked by further analysis of the separate solutions by the weight residue method, or by the silver chloride method in the case of the very dilute solutions. The recommendations of Richards³² were also followed in the analysis by the silver precipitation method. When the latter analyses were made, enough solution was used, so that an error of two-tenths of a milligram in the weighing of the silver chloride precipitate would correspond to less than 0.10 per cent error in the amount of sodium chloride. The weight of the silver chloride precipitate was found by difference with another Gooch crucible as a counter-poise. The second analysis, made upon each solution directly, was always a little higher, never more than 0.10 per cent, than the result obtained by weight dilution of the original one molal solution, apparently due to the presence of a small amount of material in suspension in the relatively large amount of water present in the solution which was used for analysis. The molalities used in the heat of dilution calculations were those calculated from the weight dilution of the standard one molal solution.

The steps involved in the calculations of the value of the function $\Delta\phi_H/\Delta(m^{0.5})$, have already been shown in connection with the sample record of a dilution experiment. The apparent molal heat content of any solute is defined by Lewis and Randall in the

³¹ Richards and Hall, J.A.C.S., 51, 709 (1929).

³² Richards and Willard, J.A.C.S., 32, 28-29 (1910).

following manner:³³

$$\phi H = (H - n_1 H_1) / n_2 \quad (33)$$

The change in the apparent molal heat content for a change in concentration from m_1 to m_2 is:

$$\Delta \phi H = (\phi H)_{m_1} - (\phi H)_{m_2} \quad (34)$$

$\Delta \phi H$ is determined by the division of the energy change involved in the calorimeter by the number of moles of solute used in the experiment. The latter result divided by the corresponding change in $\Delta(m^{0.5})$ yields the chord shown in column 9. It is these chords which are plotted as a function of $m^{0.5}$ in Figure 8.

Young and Vogel³⁴ and Machin,³⁵ in this laboratory, have measured heats of dilution for sodium chloride from a concentration a little greater than 0.10 m up to a concentration of about 5 m. Three sets of measurements made by Machin and used to establish his derivative curve in the dilute range are included in Figure 8. After the completion of this experimental work, Gulbransen and Robinson³⁶ published heat of dilution data of sodium chloride. For purposes of comparison these data have also been included as dashed lines in Figure 8.

The chords of the author are so short that they appear almost as points. For most of the experiments, the water for the dilution was placed in the diluting pipette. This caused only a 10 per cent increase in the volume of the solution, and this accounts for the very short chords. To obtain two long chords, for very low concentrations (0.01 m), the salt solution was placed inside the pipette and water outside. The change in volume for the

³³ Lewis and Randall, op. cit., p. 35.

³⁴ Young and Vogel, op. cit., pp. 3030-3040.

³⁵ Machin, op. cit.

³⁶ Gulbransen and Robinson, J.A.C.S., 56, 2637-2641 (1934).

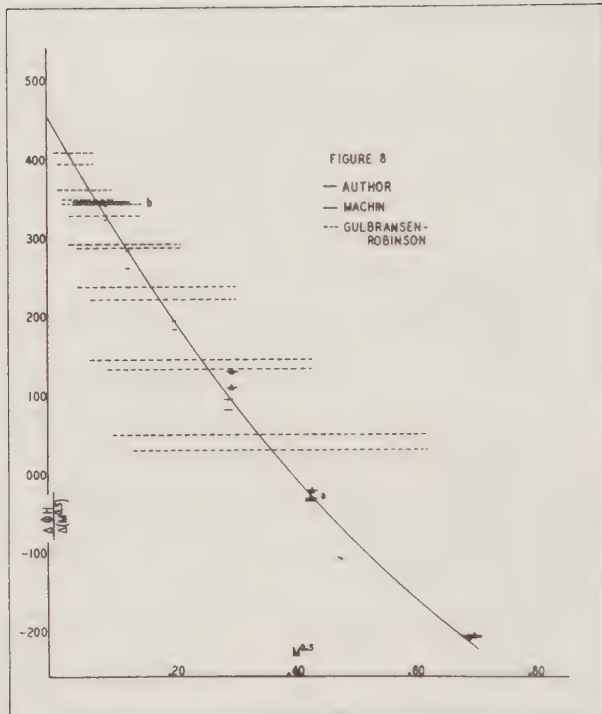


Fig. 8.--Experimental values of $\Delta\phi H / \Delta m^{0.5}$ as a function of $m^{0.5}$. A chord of the author coincides with a chord of Machin at the point a; a long chord of the author partly superimposes a chord of Gulbransen and Robinson at the point b.

solution in this case was about ten to one and resulted in a long chord. Lange, Robinson, and their coworkers placed salt solutions within their pipettes. The use of long chords complicates immensely the derivation of the various thermodynamic quantities to be derived from the heat of solution data.

The function, $\Delta\phi_H/\Delta(m^{0.5})$, between any two values of $m^{0.5}$ is the average of the slope of the true derivative curve,

$$S = d\phi_H/d(m^{0.5}) \quad (35)$$

The curve through a chord should be so drawn that perpendiculars extended from the ends of the chord to the curve should enclose equal areas between the chord and the curve. In order to evaluate S , then, it is necessary to transform the plot of chords in Figure 8 into a plot of points. The difficulty of this procedure increases with the length of the chord. The mid-point of a very short chord nearly coincides with the intersection of the chord and curve.

Gulbransen and Robinson give 418 as the limiting slope of the derivative S at 25 degrees, a value which is distinctly lower than would be expected from the application of the equation of Debye-Hückel (equation 1). Young and Gronier have utilized these long chords to calculate a limiting value for A in equation 2 by combining the method of Young and Vogel with the method of least squares. They obtained the following theoretical equation to represent the slope of S :

$$S = 462.0 + 1338.3 m^{0.5} + 550.0 m \quad (36)$$

The locus of this equation is shown on Figure 8. The result for the limiting value from equation 36 is 462 calories per mole. This is 10 per cent larger than the value reported by Gulbransen and Robinson applying a less precise method to the same data. If short chords had been used, a much less elaborate method would

have led without ambiguity to approximately the same result.

One of the objectives of this research was to verify experimentally the predictions of the Debye-Hückel theory concerning the magnitude of the limiting value for S in equation 36 in the case for sodium chloride, a typical uni-univalent electrolyte. The heat of dilution data represented by this work, combined with three sets of points from the work of Machin in this laboratory, extends from $m = 0.5$ to $m = 0.01$. The extrapolation of the curve representing these data from a value of $m^{0.5} = 0.10$ to infinite dilution yields a value for the limiting slope of about 470 calories per mole. This limiting slope can be calculated from theoretical considerations by the application of equation 1. The constant A in equation 2 includes no less than eight different physical constants. All of these are known to a high degree of precision with two exceptions, the dielectric constant for water and its temperature coefficient. The published values for the dielectric constant show a variation of about 4 per cent. The reported values for the temperature coefficient differ so much that variation from the average of the reported values is as large as 30 per cent. The constant dD/dT is reported to only one significant figure in the International Critical Tables because of the uncertainty in this value at the time of publication. Calculations of the numerical value of the expression $[1 + (T/D)(dD/dT)]$ appearing in equation 1, and based upon the widely divergent values for the dielectric data for water³⁷ reported in the literature result in values differing by as much as a factor of two or three. This would cause a similar variation of the value of the limiting slope. Apparently the best of the

³⁷Cf. Drude, Wied. Ann., 59, 48 (1896); Kockel, Ann Physik., 77, 417 (1925); Int. Crit. Tables, 6, 78 (1929); Guthbertson and Maass, Phys. Rev., 35, 613 (1930).

dielectric data on water is that of Wyman.³⁸ With Wyman's data, Harned and Ehlers³⁹ obtain 478 as the value of A.⁴⁰ Gulbransen and Robinson, also using the data of Wyman, report 480. The value of 492 is reported by Gatty.⁴¹ The value of A based on the dielectric data of Drude⁴² is 457. Under these circumstances, the value of A found in this work may be said to be in good agreement with the predictions of the theory of Debye-Hückel.

SUMMARY

I. The following advances in calorimetry have been realized experimentally:

1. A calorimeter has been designed capable of the measurement of the very small temperature differences that occur when solutions with concentrations as low as 0.01 m are diluted with water. These temperature changes approach 1×10^{-5} degrees.
2. A potentiometer has been designed to measure potentials as small as 1×10^{-8} volts. With appropriate changes in the circuit, this voltage sensitivity can be made even greater. Previous to this time, workers in this field used a galvanometer as a deflection instrument. Their procedure required the use of an electric heater in the reference half, which was used when the temperature effect was large enough to cause the deflection to exceed the limits of the galvanometer scale. The auxiliary heater

³⁸Wyman, Phys. Rev., 35, 623 (1930).

³⁹Harned and Ehlers give the value of $\bar{L}_2$ in infinite dilution as 717. A is two-thirds of this value.

⁴⁰Ibid., p. 2188.

⁴¹Gatty, Phil. Mag., (7), 11, 1082-1089 (1931).

⁴²Lange and Robinson, op. cit., p. 92.

with its attendant timing and current measuring system is eliminated when the galvanometer is used in conjunction with a potentiometer.

3. An eliminator switch which is an integral part of the potentiometer system has been designed and perfected. The use of this switch renders negligible the effect of parasitic e.m.f.'s, which effect very sensitive galvanometers.

II. From a study of the factors involved in micro-calorimetry, the following general guiding principles have been shown to apply in this kind of work:

1. The number of junctions to be used in the thermel is determined by the maximum permissible rate of heat loss in the dilution vessel; i.e., the temperature sensitivity is directly proportional to the square root of the heat loss per degree in unit time. The galvanometer should, therefore, be selected to match the resistance of the thermel.

2. The temperature sensitivity for a combination of a sensitive galvanometer and thermel depends upon the function,

$$\frac{e}{\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}}, \text{ the merit factor for the thermel.}$$

The merit factors for some common thermel pairs are listed.

3. It is possible to have high temperature sensitivity with a comparatively small number of junctions in the thermel. One hundred junctions were used in this work, but a much smaller number probably could be used, since there is now a galvanometer available with a resistance as low as one ohm. The use of a small number of junctions simplifies immensely the building of a micro-calorimeter.
4. It is possible to design and use a pipette which can be

opened with no measurable heat effect.

III. Heat of dilution data for solutions of sodium chloride as dilute as 0.01 m have been obtained experimentally. The data yielded very short chords and the curve based upon these chords yields directly the value of the limiting slope of the function $d\phi_H/dm^{0.5}$. The value of the limiting slope agrees with Young and Gronier's recalculation of the limiting slope from the data of Gulbransen and Robinson, and also with the predictions based upon the theory of Debye-Hückel when used with the dielectric constant data of Wyman.

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